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Development and Application of Newly Synthesized Guar gum Diamino Benzoic Acid (GDABA) Resin for Elimination of Hazardous Waste Metal Ions from Industrial Effluents

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ABSTRACT

The newly synthesized Guar gum Diamino Benzoic Acid (GDABA) resin for elimination of hazardous waste metal ions was developed from industrial effluents. The gaur gum has been studied for their good metal sorption properties and found to have potential for waste management. In the laboratory, chemically produced Guar gum Diamino Benzoic Acid (GDABA) derivative has been employed for the elimination of Pb^{2+}, Cd^{2+} and Zn^{2+} ions from effluents of Steel Industries in Jodhpur, Rajasthan (India). These groups of ion exchanger constitute new category of newly reformed ion exchange resin for the retraction of ions of harmful metal. It was further diagnosed by computing its thermal and FT-IR spectral analysis, ion exchange capacity etc. The estimation of 'K_d' values of these unsafe metal ions was also done at various values of pH.

Keywords: Derivative, Ion exchangers, Hazardous metal ions, Guar gum Diamino Benzoic Acid.

INTRODUCTION

Inorganic or organic hybrid ion exchange materials provide a way to integrate various useful properties into a single molecule polysaccharide[1]. Due to the presence of a great number of hydroxyl groups on polysaccharide molecules, which can bind firmly to other exchange ions through hydrogen bonds. Polysaccharide as natural polymers can make a lot of ion exchange resins[2]. Due to presence of various glycosidic linkages and monosaccharide composition, polysaccharides have unique functional characteristics and biological activities, for example amino groups provide antibacterial properties of chitosan[3] and antioxidant property is provided by sulphate groups[4,5]. In recent times, water pollution has become a serious problem worldwide. A restriction on the discharge of untreated wastewater into rivers, seas, sewers, or land has been imposed by various regulatory agencies. Different methods[6] like ion exchange methods[7-11], advanced oxidation processes[12,13], chemical and electrochemical techniques[14], solvent extraction[15,16], precipitation[17], ultra-filtration and reverse osmosis[18-20] have been employed for the elimination of hazardous metal ions from the wastewater. Hydroxybenzoic acid group has been incorporated onto guar gum by modified Porath's method of functionalization of polysaccharides[21]. The relevant work conducted by various researchers over the past few decades and discussed the structure, properties, and different modifications methods employed to develop versatile guar gum-based adsorbent[22].

Object

The aim of this work is to produce and characterize guar gum diamino benzoic acid resin using guar gum as a natural polysaccharide and diamino benzoic acid as the functional group and to use it to remove hazardous metal ions from wastewater and industrial effluent. The purpose of using Guar gum here as the polysaccharide matrix and its easy availability from agricultural resources and effective and low-cost procedures of handling and decontamination of industrial wastewater.

MATERIALS AND METHODS

Materials

The chemicals used in the synthesis of resin are tabulated in Table 1.

Table 1: Materials used for development and application of newly synthesized Guar gum Diamino Benzoic Acid (GDABA) resin

S. No	Chemical	Specification
1	Guar gum	Ases chemical works, Jodhpur
2	Dioxane (AR)	S.D fine chem. Pvt. Ltd. Boisar
3	Sodium hydroxide (AR)	Sarabhai M. Chemicals, Baroda, India
4	Epichlorohydrin (AR)	Loba Chemie Pvt. Ltd, Mumbai
5	Methanol (AR)	E Merk. Bombay, India
6	Hydrochloric acid (AR)	Sarabhai M. Chemicals Baroda, India
7	Diamino benzoic acid	Sigma Aldrich Chemicals Private Limited

Synthesis of Guar gum Diamino Benzoic Acid

The procedure followed to synthesize guar gum diamino benzoic acid is as follows:

Preparation of epoxy propyl ether of diamino Benzoic acid

A solution of 7.6 g of diamino benzoic acid (0.05 moles) in methanol was taken in a round bottom flask and 4 gm of NaOH (in minimum amount of water) was mixed into it, followed by addition of 4.65 mL (0.05 mole) of epichlorohydrin to the reaction mixture with continuous stirring on a magnetic stirrer for about 4.5 h at 60°C.

Preparation of Guar gum Diamino benzoic acid resin

81 g of guar gum (0.5 moles) was mixed with dioxane in a round bottom flask and then it was allowed to react with the prepared epoxypropyl ether of diamino benzoic acid with continuous stirring for another 4.5 h at 60°C temperature. This reaction mixture was kept for 24 hours. The resultant product was first filtered under vacuum then it was followed by washing with methanol and HCl to neutralize excess NaOH and to eliminate inorganic contaminants and then dried. The yield of Guar gum Diamino Benzoic Acid resin is 92.4 gram.

EXPERIMENTS

Preparation of stock solutions of metal ions

Zinc acetate Zn(II)

3.357 g of zinc Acetate ($Zn(CH_3COO)_2$) was dissolved in a few ml of acetic acid & volume was made up to 1000 volumetric flask to give 1000 ppm zinc solution.

Cadmium sulphate Cd(II)

2.015 g of $CdSO_4H_2O$ was dissolved in 1.5 mL conc. sulphuric acid and the volume was raised up to mark in 1000 mL volumetric flask to give 1000ppm Nickel solution.

Lead nitrate pb(II)

In a 1000 mL volumetric flask, 1.5985 g of lead nitrate was added to a small amount of concentrated sulphuric acid. The total volume of solution was made 1000 mL by pouring distilled water to the solution in volumetric flask.

Determination of ion exchange capacity

Ion exchange capacity of newly synthesized GDABA resin was estimated by direct titration with 0.11N silver nitrate solution with a 10% aqueous solution of potassium chromate solution as an indicator. Calculation of ion exchange capacity was done according to the following formula.

$$\text{Ion exchange capacity} = \frac{\text{solution volume x miliequivalents of titrant used}}{\text{volumeofaliquotex } (100-w) \text{ x wet weight of sample}}$$

Calculation of distribution coefficient by batch method

The molar distribution coefficient 'K_d' value of Zn(II), Pb(II), and Cd(II) ions was calculated by using batch method. 25 mg of Guar gum Diamino benzoic acid was taken in a glass stoppered conical flask which was containing 1 mL of 1000ppm metal solution analogous to 1 mg metal ions. In it suitable buffers were added for pH adjustments. After this the contents of conical flasks were then allowed to stir on a magnetic stirrer and then equilibrated. The two phases obtained on equilibration were then separated by using Whatman 42 filter paper and a portion of filtrate obtained was examined for the concentration of metal in filtrate.

Calibration curves were plotted for various metals, through the examination of standard solution series of metal ions with the help of atomic absorption spectrophotometer. Air acetylene flame and different wavelength of main resonance line were used for the estimation of various metals. The respective distribution coefficients were calculated by the using the following formula.

$$K_d = \frac{Amount\ of\ metal\ ion\ in\ resin \frac{phase}{gm} of\ dry\ resin}{Amount\ of\ metal\ ion\ in \frac{solution}{ml} of\ solution}$$

Elemental analysis

Estimation of nitrogen content

1.288% of nitrogen was estimated in GDABA resin using Kjeldahl's technique of quantitative nitrogen analysis.

Determination of nitrogen content

Kjeldahl's technique was used to determine the nitrogen concentration of the newly created resin. 0.2 g of GDABA resin were vacuum dried and placed in a Kjeldahl flask. To this, 10 cm^3 of concentrated hydrochloric acid (10N) then added, followed by 0.5 g of catalyst (produced by grinding 5 g of metallic selenium, 120 g of $CuSO_4$, and 150 g of potassium sulphate into a homogenous mixture). The resultant mixture was heated continuously over 2 h to produce a clear translucent solution. For quantitative ammonia measurement, the clear transparent solution was super cooled & transferred to a distillation device with 30 cm^3 of water. To get the total volume in the flask equal to 75 cm^3, 12 cm^3 of 10M NaOH was added to it. In a receiver with 4-5 drops of indicator and 5 cm^3 of 4 percent boric acid, the freed ammonia was distilled in steam for 5 minutes. 75 g of bromocresol green & 50 g of methyl red are mixed in 100 cm^3 of ethanol to make the indicator. The distilled ammonia was titrated against 0.04M HCl.

Nitrogen content in GDABA resin

Amount of resin=200 mg and Volume of 0.04 M HCl consumed=4.8 mL, Estimation of %Nitrogen content ((volume of HCl with sample-volume of HCl with blank) x normality of standard HCl x 14 x 100))/(weight of sample) =((5.6 – 0.8 mL) x 0.04 Nx14x100))/(200 mg)=1.288%

Zinc, Zn(II) ion chelation on GDABA resin

Appropriate quantities of 0.2 Molar CH_3COOH and 0.2 Molar CH_3COONa were taken in a glass stopper conical flask to obtain solutions in the range of 2-7 pH and solution of pH 8 was obtained by mixing 0.2 ammonium hydroxide and 0.2 M ammonium chloride in a conical flask. After this 0.085 g of newly developed GDABA resin and 1 mL of freshly prepared 1000ppm Zn(II) solution were added to each flask containing different pH solutions. These contents were allowed to mix completely on a magnetic stirrer and then filtered. The resulting filtrates were examined for zinc.

Lead, Pb(II) and cadmium, Cd(II) ion chelation on GDABA resin

Similar procedure was followed for chelation of lead and cadmium ions on GDABA resin as that for Zinc ions. The results obtained were summarized in the given Table 1.

Determination of moisture content

5 g of properly washed and dried resin was converted to its hydrogen form and then it was allowed to completely dry in oven at 80^0C for a day. The completely oven dried resin was again weighed. The difference of weight gives the amount of moisture content in the resin.

pH analysis

Batch method was employed to study the effect of structure of ionic polymer on its chemical behavior. For this purpose, equilibrium pH titration curve was plotted. The newly derived derivative was converted to its hydrogen ion form to eliminate the extra amount of acid followed by washing and drying overnight at 50^0C. 0.1 g of resin was taken in 8-9 flasks followed by addition of 1 N NaCl in successively decreasing amount and 1N NaOH in successively increasing amount. After this required amount of deionized water was added to maintain 25 mL volume of solution in each flask. These flasks were closed tightly and equilibrated on a magnetic stirrer to obtain constant final pH of the solution. The obtained values are listed in Table 2 and a pH titration curve plotted and is shown in Figure 1.

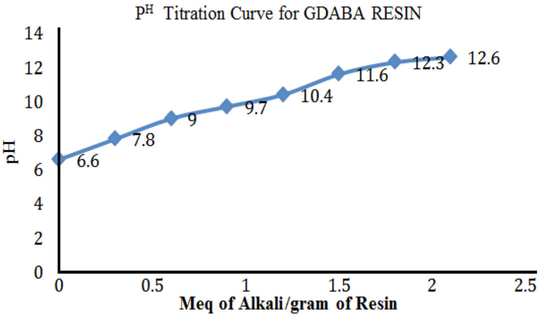

Fig. 1. pH titration curve for GDABA resin

Table 2: pH titration of GDABA resin

Flask No.	Volume of 0.1 N NaOH (mL)	Volume of 1 N NaCl (mL)	Volume of deionized water (mL)	Final pH
1	0.0	1.4	23.6	6.6
2	0.3	1.2	23.5	7.8
3	0.6	1.0	23.4	9.0
4	0.9	0.8	23.3	9.7
5	1.2	0.6	23.3	10.4
6	1.5	0.4	23.1	11.6
7	1.8	0.2	23.0	12.3
8	2.1	0.0	22.9	12.6

RESULTS AND DISCUSSION

FTIR characterisation

The FTIR spectrum of GDABA resin shows a broad peak at 3600–3200 cm^{-1}, which is due to -OH stretching. The peak at 2881.2 cm^{-1} is observed for C-H stretching vibration and another peak at 1384.2 cm^{-1} is observed for C-H bending. A C=O stretching vibration is detected at 1558.0 cm^{-1} for carboxylic group. The C-O group stretching vibration is observed at 1010.1 cm^{-1}, which is a strong peak. The C-N stretching bend was observed at 1211.4 cm^{-1} for amine group. The Fig. 2 shows the FTIR spectrum of GDABA resin.

Distribution coefficient of ZINC(II), LEAD(II) and Cadmium(II) metal ions from industrial waste

GDABA resin is profoundly selective for the elimination of hazardous metal ions from the industrial waste. On studying the results obtained, it can be inferred that with increasing pH, the 'K_d' values for different metal ions first increases to a maximum value and then decreases and it can also be inferred that the optimum results are obtained at pH 4-5. The Table 3 shows the 'K_d' values of these metal ions at pH 2 to 8. The trend of values of percent adsorption of metal ions by GDABA resin at the corresponding pH values where maximum adsorption of lead, zinc and cadmium ion takes place on newly synthesized GDABA resin is as mentioned in Table 4.

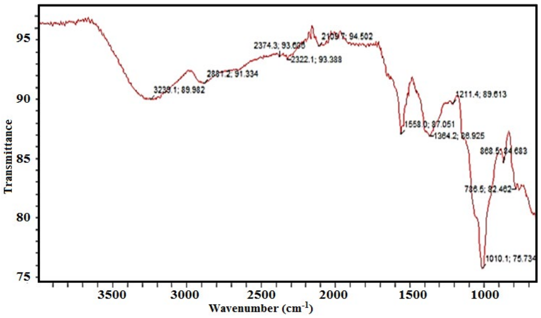

Fig. 2. Ftir characterization of guargum diamino Benzoic acid (GDABA) resin

Table 3: 'K_d' values of metal ions

pH	Zn (II)	Pb (II)	Cd (II)
1	1130.53	528.90	534.95
2	1411.57	814.71	1040.68
3	2458.23	4408.34	2167.07
4	3866.67	2181.28	1966.54
5	2981.66	1824.45	1437.21
6	2249.52	1614.70	1106
7	1781.9	1004.67	535.71

Table 4 : Percent adsorption of metal ions from effluent of industry by GDABA resin

pH	Zn (II)	Pb (II)	Cd (II)
1	70.15	52.15	49.35
2	74.59	62.81	60.88
3	83.58	89.93	79.64
4	88.74	81.58	78.17
5	86.17	79.09	72.22
6	82.22	76.86	66.36
7	78.76	67.47	49.42

Moisture content

The weight of completely oven dried resin was found to be 4.5 g which indicates the presence of 0.5g or 10% moisture.

Effect of pH

On studying the pH titration curve (Fig. 3-6) obtained for GDABA resin, it can be inferred that this resin is stable over a wide pH range of 6 to 12.

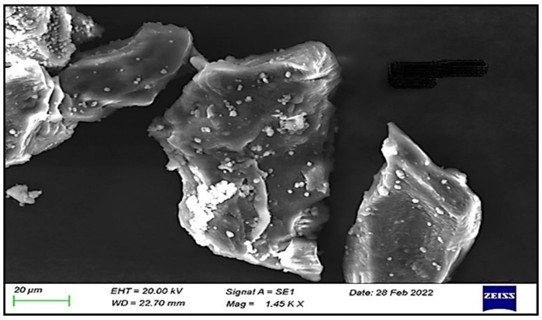

Fig. 3. Characterization of the GDABA resin: SEM images

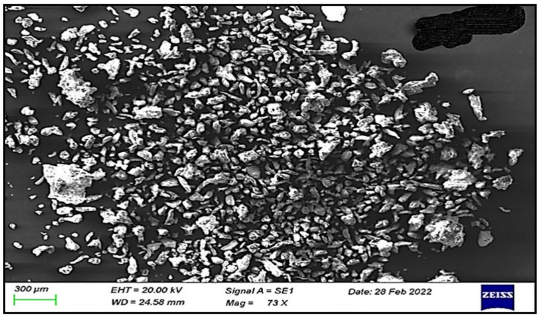

Fig. 4. Characterization of the GDABA resin: SEM images

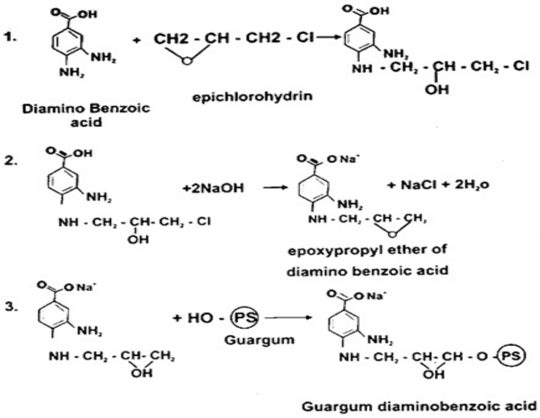

Fig. 5. Reaction scheme for synthesized Guar gum Diamino Benzoic acid (GDABA) resin

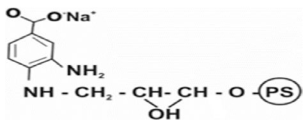

Fig. 6. Structure of Guar gum Diamino Benzoic acid (GDABA) resin

Ion exchange capacity of GDABA for the metal ions

Ion exchange capacity of GDABA resin was 10.440 mg/g for Zn(II) ion, 10.570 mg/g for Pb(II) ion and 10.618 mg/g for Cd(II) ion.

CONCLUSION

The maximum adsorption of lead and cadmium ion were observed at pH 4 and for zinc (Zn^{2+}) ion maximum adsorption was observed at pH 5. So, the separation of these metal ions from others can be done effectively at pH 4 and 5. The removal of heavy metal ions by Guar gum Diamino Benzoic acid is now considered as one of the most promising technique due to cost effectiveness, eco friendliness and rapidness. On the basis of the research work done it can be concluded that GDABA resin can selectively eliminate toxic metal ions like zinc, lead and chromium from industrial waste water. It can also be used as an effective ion exchange for heavy metals like zinc, copper, cadmium, chromium, lead arsenic etc. The newly synthesized GDABA resin is hydrophilic and biodegradable so that after effluent treatment, used resin can be easily disposed off without facing any environmental problem. Thus, present investigation reveals that newly synthesized Guar gum Diamino Benzoic acid Resin can be effectively used for removal of toxic heavy metal ions from industrial effluent.

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